

THE FICK EQUATION OF DIFFUSION

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THE FICK EQUATION OF DIFFUSION

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ABSTRACT. The diffusion and volumetric behavior of nitrogen-carbon dioxide systems near the critical point of the liquid-gas equilibrium is investigated. It is shown that the molar volume of mixtures changes sharply in certain ranges of composition. As a result diffusion takes place from smaller volume concentrations of the component to larger ones and it becomes impossible to use Fick's law to describe the diffusion process.

The diffusion rate is usually described by the well-known Fick equation /101*

$$dm/dt = -DS \text{ grad } C, \quad (1)$$

where m is the amount of material which has diffused during the period of time t ; D is the diffusion coefficient; S is the area of the diffusion cross section; C is the volumetric concentration of the diffusing component.

According to the above equation the diffusion coefficient is a positive quantity differing from 0 and infinity. In the past there was an opinion that the diffusion coefficient does not depend on the concentration of the solution. However subsequent investigations showed that this proposition is true only in very dilute solutions. In the general case the diffusion coefficient is a function of the solution composition. A good molecular-kinetic explanation of this is given by the Einstein equation (ref. 1).

The investigations of molecular diffusion near the critical point for the separation of two liquid systems into layers (ref. 2) have shown that the diffusion rate at the critical point is equal to zero. This phenomenon cannot be explained by assuming that the diffusion coefficient has become equal to zero. Such an explanation is devoid of physical meaning. The phenomenon is explained by the thermodynamics of irreversible processes which establishes that the motive power for diffusion is the gradient of chemical potential (ref. 3). Since the derivative of the chemical potential of a component with respect to its composition and consequently the gradient of the chemical potential are equal to zero at the critical point of a binary solution, the diffusion rate is also equal to zero.

The authors encountered a new interesting case when investigating the liquid-vapor equilibrium in gases compressed near the critical point for the case of nitrogen-carbon dioxide system. The variation in volume as a function of composition was investigated for this system and this variation is shown graphically in figure 1a for 15°C and a pressure of 105 atmospheres. As we can

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see from the graph there are certain compositions for which the molar volume changes sharply. This concentration dependence of the volume on the molar portion of the component leads to a complex variation in the volumetric concentration of the component as a function of the molar fraction (fig. 1b). Thus along the region AB of the curve diffusion takes place from A to B. If the Fick equation is to explain this case the diffusion coefficient must have a negative value. At the point A, where $dC/dN=0$, the diffusion rate (according to Fick) must be equal to zero. However diffusion, of course does not cease at this point. This makes us assume that the diffusion coefficient has become equal to infinity which again is devoid of any physical meaning. However all of these ambiguities disappear if we assume that the motive power for diffusion is the chemical potential gradient of the component rather than the gradient of the volumetric concentration.

/102

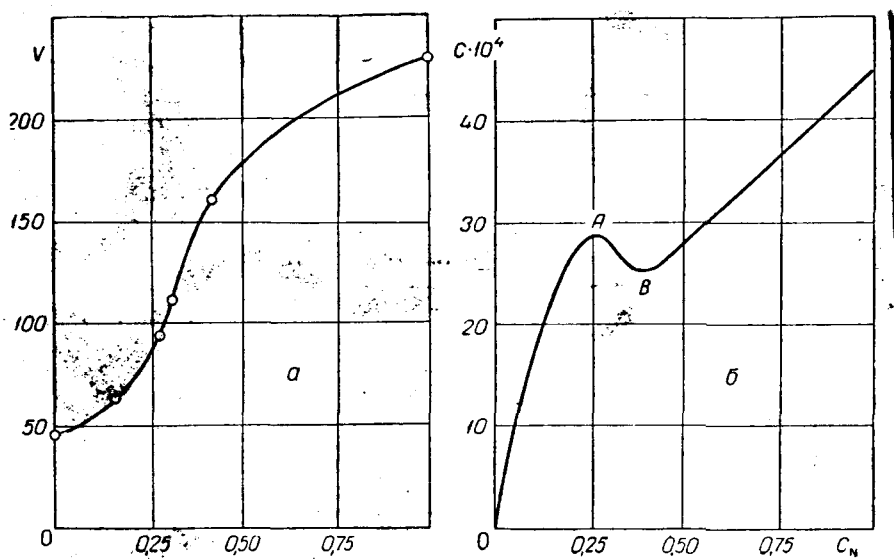


Figure 1. Variation in the molar volume V (in cm^3/mole) of a binary gaseous mixture (a) and the volumetric concentration of nitrogen C (in mole/cm^3) in this mixture (b) as a function of the composition C_N (in mole portions)

near the critical point of liquid-vapor equilibrium.

The dependence of the molar volume of a binary gas mixture on the composition near the critical point of liquid-vapor equilibrium (near the critical point of the pure solvent) (fig. 1a) does not only exclude the use of Fick's law for carrying out computations but produces a general complexity in the interpretation of results obtained from the investigation of molecular diffusion. In this region of compositions where there is a sharp change in the volumes of the mixture, a change in the concentration produced by molecular diffusion must inevitably produce convective diffusion.

The authors feel that it is necessary to devote attention to these interesting facts because the variation in the molar volume of a gas mixture as a function of composition is not limited to the nitrogen-carbon dioxide system.

This type of concentration dependence for the molar volume is common to all gaseous solutions near the critical point of the pure solvent. A thermodynamic explanation of this is given in reference 4.

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